Synthesis and characterization of Sn and Al doped ZnO nanostructures thin films and its applications in gas sensor

A synopsis submitted

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INTRODUCTION

The evolution of semiconductor science has turned up the entire world to be immensely dominated. The personal and professional needs of every human being today are deeply blended with the semiconductor technology. Engineered nanomaterials have become a core part of materials research and development in the recent decades. When the dimensions of the material microscopic structure decrease to below 100 nm their chemical and physical properties undergo significant changes. Nanoparticles (NPs) are tiny particles having a size less than 100 nm. They behave very differently due to high surface area to volume ratio properties, which provide the NPs with distinct electrical, thermal and magnetic properties. In general, properties of nanostructures vary in terms of size, shape, morphology, and crystal orientation. Apart from these, synthesis methods also play a vital role in tailoring the properties of NPs [1].

Zinc oxide-based nanostructures are one of the active components in research with a vast application in scientific fields. As a result of doping with appropriate materials, the significant variation in oxygen vacancy, band gap, and conductivity have been reported extensively. In recent years, zinc oxide (ZnO) NPs have gained great attention due to their versatile applications in various fields owing to their optical and electronic properties, and due to their ease of transforming into different morphologies. The use of these NPs in the semiconductor and electronics industries has grown tremendously. ZnO has a wide band gap of $\sim$3.37 eV and a large exciton binding energy of 60 meV [2]. ZnO has been classified as semiconductor material of group II–VI in material. This has several favorable properties like high electron mobility, good transparency, wide bandgap for semi-conductivity, high roomtemperature luminescence, etc. These properties are used in applications for electrodes in liquid crystal displays as well as in energy-saving and heat-protecting windows, electronic applications of ZnO as thin-film transistors [3].

Doped Zinc oxide is one of the most popular materials to be used in visible light photocatalysis, spin sources for spintronics, nanomedicines, and electrochemical detectors [4]. To enhance the gas sensing performance various elements such as Fe, Co, Cu, Mg, Ni have been used as a dopant in ZnO nanostructures extensively.

We would like to propose transition metals such as Cu, Ni, utilized for doping of zinc nanostructure thin films and their application in gas sensing.

LITERATURE REVIEW

Nano (smaller) is interesting and improved microelectronics has overcome the boundaries in the miniaturization equipment of metal oxide semiconductor. The term “nano” refers to a number in one billion units (i.e., 10^{-9}). A nanostructure is defined by the size of the material about 100 nm in one dimension. They are differentiated into the various types such as nanoparticles, nanotubes, nanorods, nanocrystals, nanosheets, nanocomposites, etc. The nanostructures dimensions were generally classified into zero, one, two, and threedimension nanostructures [5]. In addition, 2D and 3D thin films were fabricated [6].

ZnO Thin Films

ZnO is an n-type metal oxide semiconductor belongs to II-VI, which has a wide and direct bandgap of 3.37 eV. ZnO is a monochalcogenide material which occurs as crystal, hexagonal wurtzite is the most stable form of ZnO. ZnO has been one of the most widely studied semiconductors with various applications in photovoltaics and as a photocatalyst. The lattice parameters of hexagonal ZnO with a = 0.3296 and c = 0.52065 nm.

Several techniques have been adopted to synthesize the ZnO thin films (TFs) [7], most of which require a high vacuum, high temperature, costly equipment, catalysts, and the use of toxic gas compounds. As compared to other synthesis methods, the spray pyrolysis technique (SPT) is efficient and relatively low-cost for the fabrication of ZnO TFs [8].

Ben et al. [9] focused on the photocatalytic activities of undoped ZnO, Co (1%) doped ZnO (CZO) and in (1%) doped ZnO (IZO) thin films grown on flexible PEI (Polyetherimide) substrate by spray pyrolysis. The photodegradation of crystal violet dye was investigated under UV and sunlight irradiations. Doping and excitation energy effects on photocatalytic efficiencies are discussed. All ZnO thin films show high photocatalytic efficiency up to 80% under either UV or sunlight irradiations for 210 min. However, CZO has the higher photocatalytic performance under UV irradiation. While, the photodegradation efficiency of IZO was enhanced under sunlight irradiation due to the narrowing of its optical gap. These results are discussed based on structural, morphological and optical investigations. The photocatalytic stability of ZnO films was studied as well. So, after three photocatalysis cycles, all ZnO thin films still effective.

Tarwal et al. [10] prepared ZnO TFs by SPT, and they varied the solution concentration and studied their effect on wetting properties.

Aboud et al. [11] studied the effects of metallic doping on the photoelectron\chemical properties of zinc oxide thin films have been studied. All films have been deposited using the

spray pyrolysis technique at a constant doping level of 3 wt% whereby Cu, Ni, and Pb were used as dopants. The structure of all films was studied by X-ray diffraction which showed the grain size of all doped films to be 50 nm. The energy band gap of all films was estimated using optical transmission spectroscopy. The Ni, Cu, and Pb-doped ZnO photoelectrodes were applied for the photoelectrochemical (PEC) H_2 generation from H_2O. Pb doping leads to the highest photocurrent of the ZnO photoelectrodes.

Applications of *ZnO Thin Films*

ZnO has got a wide variety of applications. ZnO has proved to be a boon for material science as it has got a combination of unique properties like UV absorption, anti-microbial properties, thermal and optical properties. Because of its diverse properties, zinc oxide is widely used in many areas such as ceramics, lubricants, ointments, adhesives or the rubber industry, paints, chemicals, pharmaceuticals and agriculture.

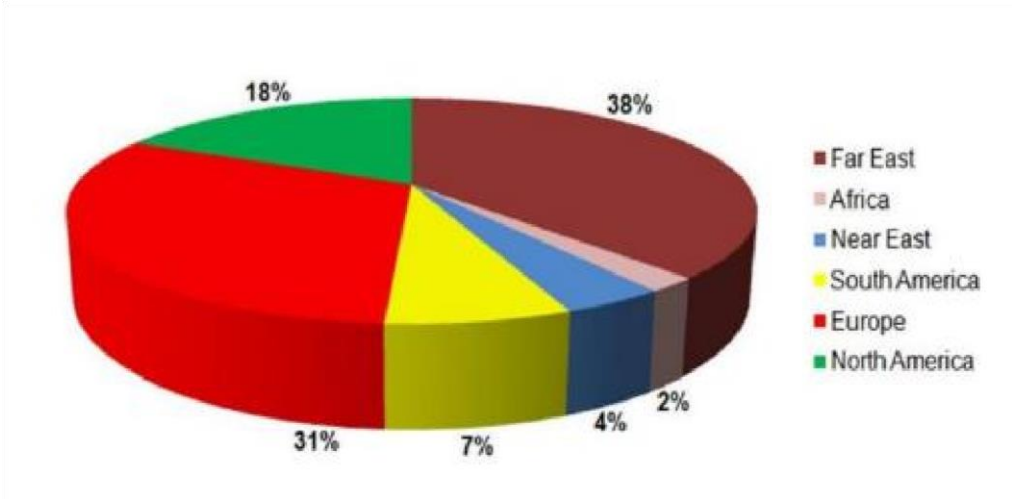

Figure 1: Global usage of Zinc oxides (ZnO)

There are many benefits to ZnO based thin films on flexible substrate, such lightweight, versatile, unbreakable and less quantity. Typically, films are used in electro optical devices and liquid crystal displays [12]. Hence, ZnO is used in this study due to many applications and advantages with low cost and high performance.

Gas Sensing

There is a strong interest in the development of wide band gap semiconductor gas sensors for the detection of combustion gases for fuel leak in spacecraft, automobiles, aircraft, fire

detectors, exhaust diagnosis and emissions from industrial processes. Diode or field-effect transistor structures are sensitive to gases such as hydrogen and hydrocarbons. These sensors have the ability to discriminate between different gases like CO, CO_2, SF_6, H_2, C_4H_{10} and C_2H_5OH.

To date, numerous functional materials have been identified with novel nanostructures consisting of subunits like TiO_2, SnO_2, ZnO, CuO, and other metal oxides. Among the above metal oxides, ZnO showed excellent properties and application in several fields including transparent electrodes, diodes, LED, sensors and solar cells, etc [13]. Also, low-temperature ZnO nanostructure can be synthesized and can control the morphology with a simple hydrothermal method. Toxic gases such as ammonia and other volatile organic compound play a vital role in polluting the environment and affecting human health. ZnO nanostructures exhibited enhanced ammonia gas sensing response compared with bulk ZnO due to high surface area and pores structure. These properties induced gas diffusion and charge transport in the gas sensor. However, still, there is some limitation in gas response at lower temperatures [14].

Hunge et al. [15] has successfully synthesized hexagonal ZnO thin films by chemical spray pyrolysis technique. Photoelectrocatalytic activity of ZnO photoelectrode is tested for photoelectrocatalytic degradation of terephthalic acid as a model organic pollutant. The degradation percentage of terephthalic acid using ZnO photoelectrode has reached up to 91% under ultraviolet illumination after 400 min. ZnO thin films are used for detecting CO_2 gas and getting maximum response for operating temperature of 350 °C and response and recovery time periods are 75 and 108 s, respectively for 400 ppm CO_2 gas concentration. ZnO sensor has good repeatability along with a quick response time. Thus, a multifunctional ZnO thin film is the potential candidate for both for photocatalytic and CO_2 gas sensing applications.

Kim et al. [16] reported the development of a-plane gallium doped ZnO, at higher temperature, whereas **Zhong et al.** [17] reported the growth of aluminium doped and germanium doped ZnO thin film in the presence of 1:3 Ar-O^2 gas pressure and at the room temperature (≈400 K).

Lupan et al. [18] prepared nanostructured ZnO thin films were deposited using a successive chemical solution deposition method and found that carbon dioxide sensitivity of Al-doped ZnO was improved by increasing surface to-volume ratio of nanostructures.

In the present proposed study, various ZnO nanostructured thin films will be studied to achieve an enhanced gas response and sensitivity at room temperature.

OBJECTIVES OF THE PRESENT WORK

The objective of the present research proposal can be summarized as follows.

1. To synthesize ZnO thin films via spray technique.
2. To fabricate transition Sn and Al-doped ZnO nanostructure thin films.
3. To investigate structural and morphological properties of prepared thin films.
4. Optical properties Sn and Al-doped ZnO thin films will be study.
5. To study gas characteristics of the prepared films.

HYPOTHESIS OF THE PRESENT WORK

- The research work is directed to obtain Sn and Al-doped ZnO thin films using spray pyrolysis technique.
- The ZnO thin films are of interest in the modern age because of its wide range of applications in solar cells, thin film transistors, biosensors, optoelectronic applications, blue-green light emitting diodes (LED) and UV photodetector applications. ZnO films will influence the physical, morphological, magnetic and optical properties will be studied.
- The comparative study of all grown crystals with the reported one may show the appreciable novelty in the different properties subjected to their applications in modern technological era.
- The enhancement in optical transmission may be studied by UV visible spectroscopy.
- The effect of doping depends on various factors such as concentration, temperature, so it is expected to grow the crystal by varying parameters and to report their influence on crystal properties.

METHODOLOGY

For the development and characterization of the samples following Work plan/method will be used:

1. **Synthesis of ZnO thin films**

Zinc oxide (ZnO) thin films were synthesized by spray pyrolysis method using an aqueous solution of zinc acetate at various concentrations.

2. Fabrication of Sn and Al-doped ZnO thin films

It is proposed to grow transition metal doped ZnO thin films by spray pyrolysis. At initial stages the efforts will be done in order to deposit good quality metal doped ZnO thin films on glass substrates.

3. Characterization of Sn and Al-doped ZnO thin films

- ***Structural Analysis:*** X-ray diffraction spectroscopy (XRD)
  X-ray diffraction (XRD) will be used to check crystallographic properties and to determine structural parameters.
- ***Morphology study:*** Field emission scanning electron microscope (SEM)
  TEM and SEM will be used to check size and shape of the nanomaterial.
- ***Elemental analysis:*** Energy dispersive spectroscopy (EDS). These techniques are used to identify and the relative compositions of elements of samples.
- ***Optical characterization:*** UV–Vis Spectroscopy, Fourier-transform infrared spectroscopy (FTIR)

  Optical absorption spectrometry is a very important tool to study the optical band gap of the films.
- ***Surface Analysis:*** Atomic force microscopy (AFM) or Brunauer-Emmett-Teller (BET) analysis

4. Gas sensing properties of the prepared thin films

- Gas sensing properties of the prepared films will be measured.

Once I started working on the objective and getting desired results of each objective will publish my research work in the reputed journals.

IMPORTANCE OF STUDY

- Zinc oxide (ZnO) is an n-type metal oxide semiconductor useful for optoelectronic device applications. Doping of transition metal ions (Cu, Ni) into ZnO lattice can lead to modification in optical, electrical and magnetic properties.

- The high melting and boiling points of ZnO make it suitable for a variety of heat treatments required for alloying purposes and device formation. ZnO exhibits extreme stability against oxidation which usually affects the device performance.
- The high cohesive energy of ZnO (1.89 eV) makes it highly stable and perhaps the most radiation resistant material amongst the direct band gap semiconductor family.
- Sn and Al-doped ZnO thin films found to be promising materials for gas sensing application. The cost-effective large-scale production of these films and the development of ZnO films with improved properties are key challenges in the field of production in gas sensors.

CHAPTER SCHEME

Chapter 1: Introduction to ZnO thin films

Chapter 2: Synthesis and characterization of thin films.

Chapter 3: Synthesis and characterization of Sn-doped ZnO thin films

Chapter 4: Synthesis and characterization of Al-doped ZnO thin films

Chapter 5: Conclusion and future scope

YEAR WISE PLAN OF WORK AND TARGETS TO BE ACHIEVE

First year:

- Course work
- Literature review
- Topic finalization and synopsis submission
- Synthesis of ZnO nanomaterials

Second year:

- Synthesis of transition metal doped ZnO thin films.
- Characterization study of prepared ZnO thin films
- Manuscript preparation and submission on the completed work

Third year:

- Gas sensing properties of prepared ZnO thin films will be studied as a gas sensing application.
- Research Publication
- Submission of the thesis for the Doctoral degree.

REFERENCES

1. Xuan L, Ju Z, Skonieczna M, Zhou PK, Huang R. Nanoparticles-induced potential toxicity on human health: Applications, toxicity mechanisms, and evaluation models. *MedComm (2020)*. 2023;4(4):e327.
2. Raha S, Ahmaruzzaman M. ZnO nanostructured materials and their potential applications: progress, challenges and perspectives. *Nanoscale Adv*. 2022;4(8):18681925.
3. eddy JR, Mani GK, Shankar P, Rayappan JB. Substrate Temperature Effects on Room Temperature Sensing Properties of Nanostructured ZnO Thin Films. *J Nanosci Nanotechnol*. 2016;16(1):489-496.
4. Reddy JR, Mani GK, Shankar P, Rayappan JB. Substrate Temperature Effects on Room Temperature Sensing Properties of Nanostructured ZnO Thin Films. *J Nanosci Nanotechnol*. 2016;16(1):489-496.
5. Barad HN, Kwon H, Alarcón-Correa M, Fischer P. Large Area Patterning of Nanoparticles and Nanostructures: Current Status and Future Prospects. *ACS Nano*. 2021;15(4):5861-5875.
6. Sheng Bi, Yu Li a, Yun Liu, Zhongliang Ouyang, Chengming Jiang. Physical properties of 2D and 3D ZnO materials fabricated by multi-methods and their photoelectric effect on organic solar cells. *Journal of Science: Advanced Materials and Devices*. 2018;3:428e432.
7. Rabeel M, Javed S, Khan R, et al. Controlling the Wettability of ZnO Thin Films by Spray Pyrolysis for Photocatalytic Applications. *Materials (Basel)*. 2022;15(9):3364.

8. Navidpour, A.H.; Hosseinzadeh, A.; Zhou, J.L.; Huang, Z. Progress in the Application of Surface Engineering Methods in Immobilizing TiO2 and ZnO Coatings for Environmental Photocatalysis. *Catal. Rev. Sci. Eng*. 2021:1-52.

9. Ben Ameur S, BelHadjltaief H, Duponchel B, et al. Enhanced photocatalytic activity against crystal violet dye of Co and In doped ZnO thin films grown on PEI flexible substrate under UV and sunlight irradiations. *Heliyon*. 2019;5(6):e01912. P

10. Tarwal, N.L.; Patil, P.S. Superhydrophobic and Transparent ZnO Thin Films Synthesized by Spray Pyrolysis Technique. *Appl. Surf. Sci*. 2010;256:7451–7456.

11. Aboud AA, Shaban M, Revaprasadu N. Effect of Cu, Ni and Pb doping on the photoelectrochemical activity of ZnO thin films. *RSC Adv*. 2019;9(14):7729-7736.

12. Comini E, Baratto C, Faglia G, Ferroni M, Vomiero A, Sberveglieri G. Quasione dimensional metal oxide semiconductors: Preparation, characterization and application as chemical sensors. *Progress in Materials Science*. 2009;54:1-67.

13. Yoon Y, Truong PL, Lee D, Ko SH. Metal-Oxide Nanomaterials Synthesis and Applications in Flexible and Wearable Sensors. *ACS Nanosci Au*. 2021;2(2):64-92.

14. Lokhande SD, Awale MB, Umadevi G, Mote VD. Effect of Ni doping on structural, optical and gas sensing properties of ZnO films for the development of acetone sensor devices. *Materials Chemistry and Physics*. 2023;301:127667.

15. Hunge, Y.M.; Yadav, A.A.; Kulkarni, S.B.; Mathe, V.L. A Multifunctional ZnO Thin Film Based Devices for Photoelectrocatalytic Degradation of Terephthalic Acid and CO2 Gas Sensing Applications. *Sens. Actuators B Chem*. 2018; 274:1-9.

16. Ji-Hong Kim, Ji-Hyung Roh, Kyung-Ju Lee, Sung-Joon Moon, Jae-Won Kim, KangMin Do, Byung-Moo Moon, Sang-Mo Koo. Growth and electrical properties of nonpolar and polar Ga-doped ZnO thin films on LaAlO3 and SrTiO3 substrates.

    Journal of Crystal Growth. 2011;334(1):72-75.

17. Zhong Yan, Jian Bao, Xin-Yang Yue, Xun-Lu Li, Yong-Ning Zhou, Xiao-Jing Wu. Impacts of preparation conditions on photoelectric properties of the ZnO:Ge transparent conductive thin films fabricated by pulsed laser deposition. *Journal of Alloys and Compounds*. 2020; 812:152093.

18. Lupan O, Chow L, Shishiyanu S, Monaico E, Shishiyanu T, Şontea V, Roldan Cuenya, Naitabdi A, Park S, Schulte A. Nanostructured zinc oxide films synthesized

by successive chemical solution deposition for gas sensor applications. *Materials Research Bulletin*. 2009;44(1):63-69.

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